Renewable and Sustainable Energy Reviews 14 (2010) 1937–1947

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Review of different test methods for the evaluation of stability of biodiesel

Siddharth Jain *, M.P. Sharma

Biofuel Research Laboratory, Alternate Hydro Energy Centre, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand 247667, India

ARTICLE INFO

Article history:
Received 31 March 2010
Accepted 14 April 2010

Keywords:
Oxidation stability
Thermal stability
Storage stability
Rancimat
Karl Fischer coulometer
Oil stability index (OSI)

ABSTRACT

The vegetable oil, fats and their biodiesel suffer with the drawback of deterioration of its quality when it is in contact with oxygen unlike petroleum diesel. There are various types of stabilities like oxidation, storage and thermal, playing key roles in making the fuel unstable. The present paper is an attempt to review all type of stability measuring test methods to find out the best method for stability measurement. From the review it is found that there are several methods to measure the stability of biodiesel but two test methods emerges the most likely choice for the purpose of measurement of oxidation stability of biodiesel. These are ASTM 2274 and 743 Rancimat test. A comparison between these two shows that these may be used alternatively. Most commonly used methods to investigate the thermal stability are Rancimat test, ASTM D 6408-08, D 5304-06 and TGA/DTA. Rancimat test has been suggested as an important method to measure the thermal stability of oils, fats and biodiesel fuels.

Contents

* Corresponding author. Tel.: +91 9456382050; fax: +91 1332 273517.
E-mail address: arthjain2001@gmail.com (S. Jain).

1364-0321/$ – see front matter
doi:10.1016/j.rser.2010.04.011

1. Introduction

Numerous test procedures have been either developed or adopted to measure the various factors associated with oxidative and thermal instability of biodiesels. Such test methods can be categorized based on whether they measure initial fatty oil composition, primary oxidation products, secondary oxidation products, physical properties, or carryout stability test.

The compositional parameters pertaining to the initial fatty oil or ester include the ester content, fatty acid chain distribution within the fatty oil or ester and the type and extent of olefinic unsaturation. Special indices designed to consider the amount of allylic or bis-allylic carbons have been developed. Several methods directly measure the tocopherols or indirectly measure the impact of natural antioxidants have also been proposed. Primary oxidation products are hydroperoxides and conjugated dienes and procedures to measure both are established for fatty oils and esters. Secondary oxidation products have been measured by many procedures depending on the type of compounds of interest. Total acid number, anisidine value (aldehyde content) and an HPLC method for polymers are among the most important. An index 'TOTOX' designed to take into account both primary and secondary oxidation has also been proposed based on a weighted linear sum of peroxide value and anisidine value. Physical properties that are sensitive to fatty oil oxidation include viscosity, refractive index and di-electric constant. A number of accelerated stability test methods have been used which involve the stressing of the fatty oil or ester by combination of elevated temperature, time and enhanced oxygen exposure while measuring one or more oxidation-sensitive properties such as peroxide value, insolubles, evolution of volatile short chain acids or heat of reaction. Some of these methods include the Active Oxygen Method, ASTM D2274, ASTM D4625, oxidation stability index (OSI), or pressurized differential scanning calorimetry. The OSI test has gained acceptance in Europe where it is part of the biodiesel specification. Within the U.S. it is a common research tool. The Metrohm Rancimat apparatus is frequently used to measure OSI and the terms "Rancimat" and "OSI" are often used interchangeably in the literature while referring to the test method. However, no simple stability test or single stability parameter appears to be adequate to define all the stability characteristics of biodiesel fuel. It is highly unlikely that any single new test will be able to completely define biodiesel stability either.

2. Test methodology relating to fuel stability

2.1. Initial fatty oil composition

The ester content of a biodiesel fuel, a basic property, should be known. An earlier method using gas–liquid chromatography (GLC) has been used [1], but the standard method now used is usually a gas chromatographic procedure (Pr EN 14103 or AOCS Ce 1-62) [2] commonly called FAME (fatty acid methyl ester) analysis [3]. This procedure gives not only the percent ester in the fluid, but also the percentage of the individual esters according to their fatty acid structure.

One of the oldest and most common methods of determining the level of unsaturation in a fatty oil or ester is the iodine value (IV) [4–6]. Two ASTM methods exist for measuring this parameter, D1541 and D1959. The later determines total olefinic unsaturation only in fuels that contain no conjugated polyunsaturation while the former accurately determines the total olefinic unsaturation regardless of the isomeric configuration, but is a very tedious procedure involving a photographer's darkroom for part of the laborious sample work up. Accordingly, this procedure is seldom used in the fatty oils industry. Also, IV has been shown to be a poor predictor of relative oxidation stability of fatty oils and esters as well as the relative tendency of a biodiesel fuel to form engine deposits [7]. More specifically, IV has been shown not to correlate with OSI in a series of mixtures of pure methyl ester compounds [6].

Several more useful indices have been developed using FAME analysis results [6,7]. The allylic position equivalent (APE) is a theoretical measure of the number of singly allylic carbons present in the fatty oil or ester, assuming that all poly-olefinic unsaturation is methylene-interrupted. The bis-allylic position equivalent (BAPE) is a similar theoretical measure of the number of doubly allylic carbons present in the fatty oil or ester. Both of these indices correlate with OSI IP [6]. The BAPE, in particular, has been shown to correlate with the OSI IP with an R^2 value of 0.983. Of course, these two indices can be correctly calculated from FAME analysis only for fatty oils or esters derived from methylene-interrupted sources such as rapeseed or soy. For oils that do not have methylene-interrupted poly-olefinic unsaturation (such as jojoba oil and meadowfoam oil), the standard APE and BAPE formulae are not valid. The APE and BAPE values of such oils must be calculated individually depending on the exact known isomeric structure of the poly-olefinic unsaturation [7].

Over the last 25 years, several methods based on high performance liquid chromatography (HPLC) have been developed to measure one or more of the four isomers of tocopherol [8–11]. The HPLC method that has been used most recently in the biodiesel industry is ISO 993684 [3]. Several methods have been developed to measure the "antioxidant power" of fatty oils and esters out of which one method uses an amperiometric procedure to determine the oxidation potential of a fatty oil or ester [12]. The authors claim that the most effective fatty oil antioxidants gave oxidation potentials between +0.4 V and +0.6 V relative to an Ag/AgCl reference electrode. Two methods have been reported that use a stable colored radical that acts as a hydrogen scavenger for active hydrogen available in antioxidants. As the radical captures the hydrogen, the color is reduced and the progress of this reaction can be measured by appropriate measurements in the UV/Visible spectra. One method uses a neutral radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) [13]. While another method uses a radical cation 2,2′-azinobis (3-ethylbenzothiozoline-6-sulfonic acid) (ABTS) [14]. The main difference between the two methods is that the earlier method requires up to 6 h reaction time for the color reduction reaction to come to equilibrium. While the later method has a reaction time of about 2.5 min.

2.2. Primary oxidation products

As already discussed, primary oxidation products are characterized as conjugated diene hydroperoxides which can be

measured by ASTM D3703 or by similar procedures [15–20]. Conjugated dienes are measured by UV adsorption at 232 nm as per ISO 365650 [20,21].

2.3. Secondary oxidation products

A very sensitive wet method to detect carbonyl compounds and a UV adsorption method used to determine unsaturated carbonyls compounds have been reported [22]. The thiobariturIc acid (TBA) test was an old test to measure the levels of aldehydes produced during the oxidation of fatty oils [23]. However, the chemical reaction critical to this procedure has more recently been shown to produce significantly erroneous amounts of the final product measured during sample workup [24]. The anisidine value (AV) test (EN ISO 6885 or AOCS Cd 18-90) [25] is a more reliable method now used to determine aldehydes levels in oxidized fatty oils and esters. A similar method using benzidine instead of anisidine has been reported but was not used to any significant extent [26]. Several methods to measure volatile aldehydes in closed system headspace have also been reported [27–29].

Since oxidation is a multi-step reaction sequence involving both primary and secondary species, an index has been proposed to better track the oxidation process. This index, the TOTOX value, is defined as follows [30,31]:$\text{TOTOX} = 2 \times \text{PV} + \text{AV}$Development of acidic materials during oxidation is typically measured by simple titration such as Total Acid Number, ASTM D664 (TAN) [16,32,18,19,3]. Early methods to measure polymer levels in fatty oils and esters have been proposed [33,34]. The procedure most often used in the biodiesel industry is BS EN ISO 16931, a size exclusion HPLC procedure using a refractive index detector [3]. A similar procedure is AOCS Cd 22-91.

2.4. Physical properties

The most obvious physical property used to measure oxidation is the viscosity because the polymerization will necessarily enhance that property. Kinematic viscosity seems to be the most often used procedure [16,18,19] although absolute viscosity could also be used. Several studies have used refractive index to show the formation of polymers [22,35–37]. The fatty oil or ester polymers have higher refractive indices is undoubtedly the only reason why a refractive index detector is used in the BS EN ISO 16931 procedure. Di-electric constant has also been used as a means to measure the development of more polar oxidation products than the parent fatty oil or ester [34].

The fuel stability can be studied with respect to the following parameters.

2.4.1. Iodine value (IV)

It is one of the oldest and most common method to determine the magnitude of unsaturation in fatty oil or ester [6,4,5]. D1541 and D1959 are the two available ASTM methods used to measure IV, though it not necessarily a good method for assessing the stability as it depends on the position of the double bonds available for oxidation [7]. Knothe et al. have also showed that OSI of various FAME correlates better with respect to BAPE equivalents than IV [6].

2.4.2. Peroxide value

The peroxide value is less suitable for monitoring the oxidation as it tends to increase and then decrease due to its further oxidation to form the secondary oxidation products [38,18,39]. When the peroxide value reached a plateau of about 350 mequiv./kg ester during biodiesel (SME) oxidation, acid value and viscosity continue to increase monotonically [39]. Besides viscosity, the acid value has a good potential as a parameter for monitoring biodiesel quality during storage [31,40].

2.4.3. Viscosity

Viscosity has been found to increases with increase in chain length (number of carbon atoms) and with increase in the degree of saturation. FFAs are responsible for higher viscosity than the corresponding methyl or ethyl esters. Double bond configuration influences the viscosity, i.e., *cis* double bond configuration results in lower viscosity than *trans* while the position of the double bond affects the viscosity to less extent [41]. Since the oxidation processes lead to the formation of FFAs, isomerization of double bond, usually, *cis* to *trans* and formation of high MW products increases the viscosity with increasing oxidation. Based on the measurement of kinematic viscosities of four different biodiesel fuels and their blends with diesel, Yuan et al. [42] have found a viscosity–temperature relationship similar to diesel. Further, a relationship between viscosity and specific gravity was also developed that can estimate viscosity from specific gravity of biodiesel. The accuracy of this method was found comparable to the weighted mass based semi log blending equation.

2.4.4. Structure indices

The allylic position equivalent (APE) is a theoretical measure of the number of singly allylic carbons present in the fatty oil or ester assuming that all poly-olefinic unsaturation is methylene-interrupted. The bis-allylic position equivalent (BAPE) is a similar theoretical measure of the number of doubly allylic carbons present in the fatty oil or ester. Both APE and BAPE have been correlated with oxidation stability index (OSI) and peroxide value [6].

Knothe et al. [6] studied the influence of structure and concentration of individual fatty compounds on the oxidation stability of fatty acid esters. Other stability specifications like APE and BAPE for allylic and bis-allylic position equivalents takes into account both the number and position of double bonds in the chains. Knothe suggested APE and BAPE is better correlated to vegetable oils in terms of observed properties [6].

Knothe has suggested the following relation to determine the APE and BAPE values [12]:

$$\text{APE} = 2_x(A_{\text{C18:1}} + A_{\text{C18:2}} + A_{\text{C18:3}}) \tag{1}$$

$$\text{BAPE} = A_{\text{C18:2}} + 2 \times A_{\text{C18:3}} \tag{2}$$

where A is the amount of each fatty compound.

Jain and Sharma [43] have calculated APE and BAPE values for different oils ME using Eqs. (1) and (2) respectively and plotted the variation of induction period with APE and BAPE respectively which shows that as the APE and BAPE value decreases, the induction period increases indicating the credibility of the equations. But the value of R^2 is 0.43 and 0.22 for APE and BAPE respectively which is very less and is not always true. The reason may be that the amount of natural antioxidants is different in different oil MEs depends on the process of production and the process of distillation of biodiesel. The above results also indicate that the impact of APE is much on induction period than BAPE.

Knothe [12] has also developed a correlation between OSI & BAPE as given below:

$$\text{OSI} = 3.91 - 0.045 \times \text{BAPE} \quad (R^2 = 0.983) \tag{3}$$

A plot of BAPE vs OSI calculated using Eq. (3) for different oil ME to check the credibility of the equation has also been plotted by Jain and Sharma [43] which shows that the value of R^2 is 1 indicating that the relation is applicable to all the MEs under consideration by the authors.

The relation between the OSI and induction period shows the value of R^2 is very less (0.2172) which indicates that the relation is

not applicable to all ME. The reason may be that the amount of natural antioxidants is different in different oil ME depends upon the process of production and the process of distillation of biodiesel. Also same oil ME produced at different places may have different properties [43].

2.4.5. Oxidizability

Some authors have used another index of stability known as Oxidizability (OX) as given by [27]:

$$OX = \frac{0.02\ (\%O) + (\%L) + 2\ (\%Ln)}{100} \quad (4)$$

where O refers to oleic acid (18:1), L refers to linoleic acid (18:2) and Ln refers to linolenic acid (18:3).

The relation between Oxidizability (OX) and induction period indicates that OX decreases with increase in induction period and since the value of R^2 is very less (0.2255), the relationship therefore, is not very reliable parameter [43].

3. Various stability test methods

Various procedures designed to accelerate the oxidative and/or thermal instability of fatty oils have been developed or adopted from similar procedures used in other industries (most notably the fuels and lubricants industries).

3.1. Oxidation stability of biodiesel

Different parameters and test methods to measure the oxidation stability are given as below.

3.1.1. Active oxygen method

The Active Oxygen Method, AOM (AOCS Method Cd 12-57) [44] has been used for sixty years with different modifications [45–49]. This test procedure involves heating an oil sample at a predetermined temperature while bubbling dry air through at a set rate. The time (usually in hours) required for a specific peroxide value to be achieved is considered as the measured parameter. Sometimes, the rapid increase in PV is also used as the endpoint determination.

3.1.2. ASTM D2274, standard test method for oxidation stability of distillate fuel oil (accelerated method). Modified, specifically for use with biodiesel by NREL, USA [50]

A method similar to the active oxygen method has been developed by the petroleum fuels industry as ASTM D2274 which uses a filtration and gravimetric determination to measure the insolubles produced during a heated oxidation period in which O_2 is bubbled through the sample (typically for 16 h at 95 °C) [51]. A 350 ml volume of filtered middle distillate fuel is aged at 95 °C for 16 h. Oxygen is bubbled through the sample at a rate of 3 l/h. After aging, the sample is cooled to approximately room temperature before filtering to obtain the filterable insolubles. Adherent insolubles are then removed from the oxidation cell and associated glassware with trisolvent (a mixture of equal parts of toluene, acetone, and methanol). The trisolvent is evaporated to obtain the quantity of adherent insolubles. The sum of the filterable and adherent insolubles expressed as milligrams per 100 ml, is reported as total insolubles. As with the D4625 analyses, 100 ml of the aged, filtered fuel was mixed with 400 ml of *iso*-octane and filtered though Whatman GF/F filters (47 mm diameter) were used. After filtering the aged sample, but prior to solvent washing of the filters, an aliquot of the filtrate was obtained for additional testing. The aliquot was analyzed for total acid number (ASTM D664) and kinematic viscosity at 40 °C (ASTM D445). As an additional analysis for biodiesel-soluble polymers, 100 ml of the aged and filtered fuel was mixed with 400 ml of *iso*-octane. The aged fuel/*iso*-octane mixture was also filtered through a separate pair of filters.

ASTM D2274 indicates that the test can discriminate between very stable fuels and very unstable fuels. Unlike the Rancimat, this test does not provide any measure of induction period. It is presumed that all antioxidant capacity in the neat biodiesel is consumed during the test. Hence, this test is more a measure of the tendency of the B100 to form polymers and insolubles. For those concerned about the formation of these materials, D2274 is probably a better screening tool [50].

In general, each of the test methods showed the relative efficacy of various antioxidants. The relative ranking was similar but not always exactly the same. Test times and temperatures seem to have a significant effect with some of the tests such as D2274.

3.1.3. ASTM D3241, standard test method for thermal oxidation stability of aviation turbine fuels (JFTOT procedure) [52]

This test method measures the high temperature stability of gas turbine fuels using the Jet Fuel Thermal Oxidation Tester (JFTOT) that subjects the test fuel to conditions that can be related to those occurring in gas turbine engine fuel systems. The fuel is pumped at a fixed volumetric flow rate through a heater after which it enters a precision stainless steel filter where fuel degradation products are trapped. In this project, the precision filter had to be removed because it plugged too quickly. The apparatus uses 450 ml of test fuel ideally during a 2.5 h test. The essential data derived are the amount of deposits on an aluminum heater tube as determined by ellipsometry (an optical technique for measuring the thickness of thin films), and the rate of plugging of a 17 μ nominal porosity precision filter located just downstream of the heater tube. Because of the small sample size, the data are inconclusive and therefore further study to evaluate this test method is warranted. The JFTOT could be a significant tool for studying high temperature deposit formation with B100. However, the JFTOT is not likely to be useful as an oxidation stability test for specification purposes. Multiple tests would be required to establish the induction period of a given B100, the time and cost of which could be prohibitive.

ASTM D3241 (JFTOT) will require additional study to determine if it can be used to measure the oxidation stability of biodiesel. This test is quick and simple to perform. There are numerous methods for quantifying the deposits formed although most are visual, so not as useful. The ellipsometric tube-rating instrument shows promise since the deposit color does not affect the measurement. This test method is a specification test for aviation fuel so there is already acceptance of the results for specification purposes. The greatest strength of this test may be as a measure of the tendency of a biodiesel to form deposits on a hot metal surface. In general, there is currently insufficient data to recommend this test as a specification test but it requires further additional study.

3.1.4. EN 14112, the Rancimat test, fat and oil derivatives. Fatty acid methyl ester (FAME). Determination of oxidation stability (accelerated oxidation) test [53]

There are two new European standards for biodiesel: EN 14213, for home heating fuel and EN 14214 for automotive diesel fuel. Both of these standards have stability requirements based on the Rancimat test as given below:

- *Heating fuels*: Fatty acid methyl esters (FAME)—stability requirement: Rancimat Induction Period @ 110 °C $\geq$ 4 h.
- *Automotive fuels*: Fatty acid methyl esters (FAME) for diesel engines—stability requirement: Rancimat Induction Period @ 110 °C $\geq$ 6 h.

Because the Rancimat test is included in these two European specifications, it is in much wider use in Europe as compared to the

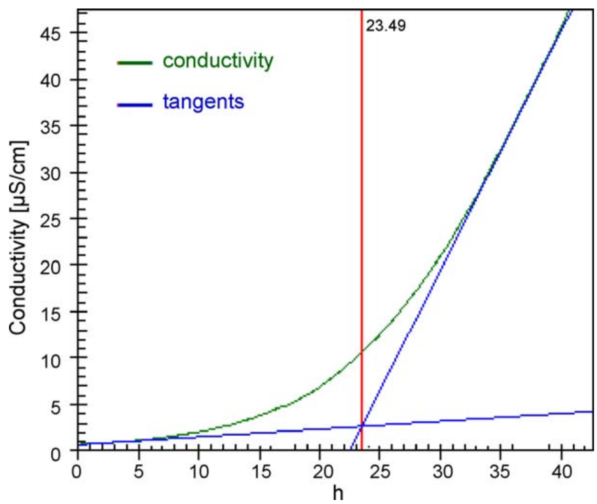


Fig. 1. Graphical determination of induction time (t) by the tangent method (manual evaluation).

United States and accordingly the quantum of data from running of the test on biodiesel samples is greater in Europe.

In Rancimat method, the oxidation is induced by passing a stream of air at the rate of 10 l/h through biodiesel sample (3 g) kept at constant temperature (100, 110 and 120 °C). The vapors released during the oxidation process together with the air are passed into the flask containing 60 ml of demineralized water and fitted with an electrode for measuring the conductivity. The electrode is connected to a measuring and recording device. It indicates the end of IP when the conductivity begins to increase rapidly. This accelerated increase is caused by the dissociation of volatile carboxylic acids produced during the oxidation process and absorbed in the water. When the conductivity of this solution is recorded continuously, an oxidation curve is obtained whose point of inflection, known as the IP, can be calculated by the point of intersection of two tangents as shown in Fig. 1.

The OSI test is the commonly used test in Europe where biodiesel fuels should meet the specification of an induction period (IP) of at least 6 h when tested at 110 °C [54]. The Metrohm Rancimat apparatus is frequently used to measure OSI and the term "Rancimat" and "OSI" are often used interchangeably in the literature while referring to the test method. OSI, commonly used in experiments, requires to pass air through a heated sample of the fatty oil or ester [55]. The air coming out of the sample is finally passed through water contained in a tube fitted with a conductivity meter (Fig. 2). A sharp rise in conductivity is interpreted as indication of the formation of short chain water soluble carboxylic acids, i.e., secondary oxidation products. Studies have indicated that the primary acidic species formed in the Rancimat OSI test is formic acid. The mechanism of decomposition of hydroperoxides to form formic acid has been explained by Hasenhuettl et al. [56].

One significant difference regarding the use of the Rancimat test in Europe vs the U.S. is that most of the B100 produced in Europe is from rapeseed oil while most of the biodiesel produced in the U.S. is made from soybeans or yellow grease. Because of its composition (lower polyunsaturated content), the rapeseed methyl ester (RME) tends to have significantly longer Rancimat induction periods than either soy or yellow grease. Typical induction periods for RME are 4–6 h as compared to 1–2 h for soy and yellow grease [57].

This test is well established in Europe and is included in several European specifications. It is quick and simple to run and could be completed in a single work shift. It provides a repeatable measure of the antioxidant capacity of the biodiesel although the relationship of that measure to the field has not been established.

Several authors have reported the work done on oxidation stability using Rancimat test. BIOSTAB [58] project has reported a comparison between ASTM 2274 and Rancimat test as shown in Fig. 3.

This indicates the relationship between the filterable, adherent and total insoluble with induction period. Fig. 3 indicates that the total insolubles and filterable insolubles are in batter agreement with Rancimat induction period. This, in turn, indicates that both the tests can be used interchangeably.

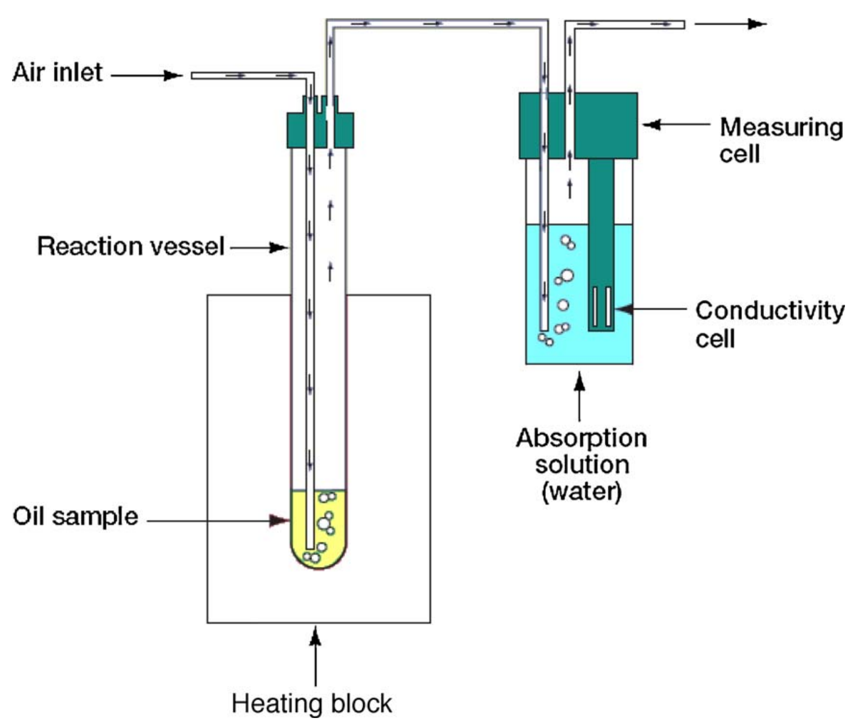


Fig. 2. Schematic of Rancimat test [55,56].

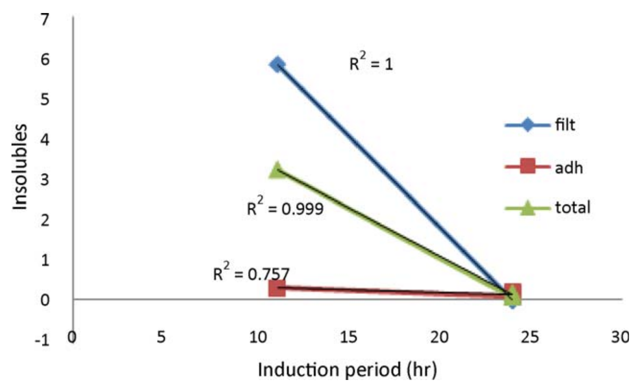


Fig. 3. Comparison between ASTM 2274 and Rancimat induction period

3.1.5. ASTM D5483, standard test method for oxidation induction time of lubricating greases by pressure differential scanning calorimetry [59]

ASTM D5483 is failed to give useful results regarding the relative stabilities of various fuels. Pressurized differential scanning calorimetry (PDSC) has been used in several studies to measure the oxidation stability of fatty oils and esters with and without added antioxidants [60–62]. When run using an isothermal procedure, the time required to detect an exothermic reaction is considered the induction time. When run using a non-isothermal procedure, the temperature, where an exothermic peak is detected, is called the oxidation temperature (OT).

3.2. Storage stability

3.2.1. ASTM D 4625–04, standard test method for middle distillate fuel storage stability at 43 °C (110 °F) [63]

Standard Test Method ASTM D4625 is the most widely accepted test method for assessing the storage stability of middle distillate petroleum fuels. The fuel is stored at 43 °C for selected periods up to 24 weeks. One week of storage in this test is generally accepted as equivalent to 1 month of storage at 17 °C (65 °F). Typically, a sample is filtered to determine total insolubles on a weekly basis. For testing of biodiesel, Whatman GF/F filters (47 mm diameter) were used. After filtering the aged sample, the filtrate was analyzed for total acid number (ASTM D664) and kinematic viscosity at 40 °C (ASTM D445).

As an additional analysis, 100 ml of the aged, filtered fuel was mixed with 400 ml of *iso*-octane to precipitate any polar polymeric materials that may have formed as a result of ageing. The aged fuel/*iso*-octane mixture was filtered through a separate pair of filters. This was done in a previous study that concluded that ageing of B100 under these conditions does not result in the formation of insolubles because the oxidized and polar polymers formed are soluble in the biodiesel. Dilution with a non-polar solvent such as *iso*-octane, was shown to result in precipitation of these polymers.

This method indicates that viscosity is not sufficiently sensitive to changes in polymer formation. Also, the conditions of this test are very mild compared to some of the other test methods often used to measure oxidation stability. This test is more representative of changes in the biodiesel during longer periods of quiescent storage, typically, at temperatures below 30 °C. It is not representative of the higher temperatures and greater oxygen exposure in a diesel vehicle fuel system.

Although, it is generally an accepted test for the storage stability of petroleum fuels, similar correlations to the storage of biodiesel have yet to be developed. Until those correlations have been developed, the ability of the test to measure storage stability is unclear. The milder conditions and very long test times used in this method make it a poor choice as a convenient and predictive measure of oxidation stability.

ASTM D4625 is an excellent method for estimating the long-term storage stability of middle distillate petroleum fuels. One week of storage at 43 °C is widely accepted as equivalent to 4 weeks at 15 °C (underground, ambient storage). While the same relationship has yet to be proven for B100, most researchers have tended to accept that the correlation holds. This makes D4625 an excellent research method but it is not acceptable as a specification test.

3.2.2. Modified Rancimat test for storage stability [20,58]

Rancimat test may also be used for testing the storage stability of biodiesel. For the purpose of checking the storage stability, it is modified by BIOSTAB project [20,58]. A stream of purified air (10 l/h) is passed above the surface of 3 g of sample heated at 80 °C during 24 h and peroxide value, ester contents and polymer content are measured. The modified Rancimat test is suitable for use in terms of repeatability, significance and is easier to handle.

3.3. Thermal stability

3.3.1. ASTM D 6468-08, standard test method for high temperature stability of middle distillate fuels [65]

Two 50-ml volumes of filtered middle distillate fuel were aged for 90 or 180 min at 150 °C in open tubes with air exposure. After aging and cooling, the fuel samples were filtered and the average amount of filterable insolubles is estimated by measuring the light reflectance of the filter pads. An unused filter pad and a commercial black standard define the 100 and 0% extremes of the reflectance rating range respectively.

The reflectance measurement works well with petroleum diesel fuel because the particles formed during the aging are typically brown or black. Hence, increased amounts of particles result in decreased reflectance. With biodiesel, the particles and polymers formed have almost no visible color. Therefore, the increased amounts of biodiesel particles/polymers result in little or no change in reflectance. This means that the test gives the best results when the biodiesel particles/polymers are measured gravimetrically.

ASTM D6468 supports the widely held assertion that the thermal stability of B100, as measured by this test, is very good. In the BIOSTAB project, both B100 and petroleum diesel samples were tested. The B100 samples had very little thermal degradation as measured either by reflectance or filter weight. However, the petroleum diesel samples showed significant differences in their thermal stability characteristics.

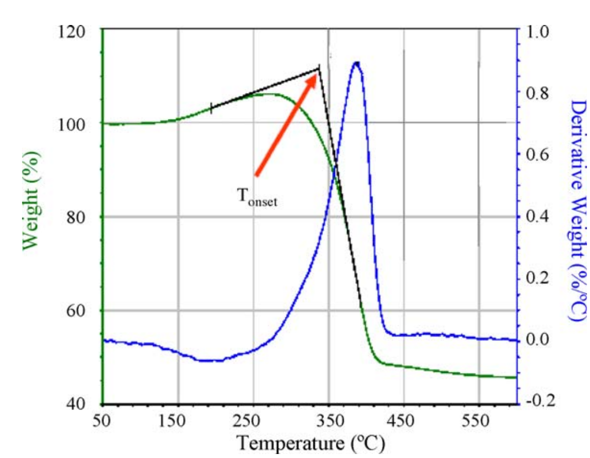


Fig. 4. TGA thermogram showing various parameters [66].

Table 1
Comparison of different test methods for stability of biodiesel.

S.N.	Type of stability	Name of test method	Stability parameter (s)	Merits	Demerits	Remark	References
1.	Oxidation	(i) Active oxygen method	Induction period	–	(a) Costly (b) Labor intensive	Not good	[44–49]
		(ii) ASTM D2274	Total insolubles, filterable insolubles and adherent insolubles	(a) The test can discriminate between very stable and very unstable fuels	(a) Unlike the Rancimat, this test gives no measure of induction period (b) Test time and temperatures seem to have a significant effect on the results and chances of error are high (c) No specification is available in any national or international standards	Good	[50,51,57]
		(iii) ASTM D3241		(a) The JFTOT could be a significant tool for studying high temperature deposit formation with B100 (b) This test is quick and simple to perform	(a) Because of the small sample size, the data are inconclusive (b) The JFTOT is not likely to be useful as an oxidation stability test for specification purposes (c) Multiple tests would be required to establish the induction period of a given B100 (d) The time and cost could be prohibitive (e) Requires additional study to determine if it can be used to measure the oxidation stability of biodiesel (f) No specification is available in any national or international standards	Not good	[52,57]
		(iv) EN 14112	Induction period	(a) Simple (b) Less chances of error (c) Repeatability is good (d) Specifications are available in ASTM and European standards related to induction period	–	Very good	[53–58]
		(v) ASTM D5483		–	(a) Do not give useful results regarding the relative stabilities of various fuels (b) No specification is available in any national or international standards	Not good	[57,59–62]
2.	Storage	(i) ASTM D 4625–04	Total insolubles, filterable insolubles and adherent insolubles	(a) The conditions of this test are very mild compared to some of the other test methods, often, used to measure oxidation stability	(a) This method indicates that viscosity is not sufficiently sensitive to changes in polymer formation	Good	[57,63]

Table 1 (*Continued*)

S.N.	Type of stability	Name of test method	Stability parameter (s)	Merits	Demerits	Remark	References
				(b) This test is more representative of changes in the biodiesel during longer periods of quiescent storage, typically at temperatures below 30 °C (c) It is an excellent method for estimating the long-term storage stability of middle distillate petroleum fuels	(b) It is not representative of the higher temperatures and greater oxygen exposure found in a diesel vehicle fuel system (c) Need of very long test times used in this method make the method a poor choice as a convenient and predictive measure of oxidation stability (d) No specification is available in any national or international standards		
		(ii) ASTM D 5304–06	Total insolubles, filterable insolubles and adherent insolubles	–	(a) No specification is available in any national or international standards	Not good	[64]
		(iii) Modified Rancimat test for storage stability	Induction period	(a) Less time consuming (b) Good repeatability (c) Chances of error are very less		Very good	[20,58]
3.	Thermal	(i) ASTM D 6468–08	Total insolubles, filterable insolubles and adherent insolubles	(a) It is very short 90-minute test which makes it very attractive test for quality assurance and quality control	(a) There is no active addition of air or oxygen to the fuel during testing this test is therefore not useful for measuring oxidation stability (b) This test method does not provide a useful discrimination between biodiesel fuels of varying quality (c) No specification is available in any national or international standards	Good	[57,65]
		(ii) Modified Rancimat	Polymers	(a) Less time consuming (b) Modified form of ASTM D6468-08 (c) Less error (d) Good repeatability	(a) No specification is available in any national or international standards	Very good	[20,58]
		(iii) TGA/DTA	Activation energy, onset temp, oxidation induction time and specific heat	(a) Less time consuming (b) High precision (c) Good repeatability	(a) Relatively costlier	Very good	[66–81]

ASTM D6468 has existed in nearly the same form (albeit different names) for over 60 years. Its very short 90-min test time makes it a very attractive test for quality assurance and quality control. The 150 °C test temperature makes this test quite severe. There is no active addition of air or oxygen to the fuel during testing so this test is not as useful for measuring oxidation stability. Also, this test method has historically relied on estimating the amount of insolubles formed based on the darkness of the material trapped on a filter pad. Biodiesel insolubles tend to be far less dark in color than petroleum diesel and as such, are more difficult to quantify using optical methods. Gravimetric measurement of insolubles provides more reliable quantification. Biodiesel tends to be very thermally stable but less oxidatively stable when compared to petroleum diesel. This test method does not provide a useful discrimination between biodiesel fuels of varying quality. This test may, however, be useful for B20 but more work is still required to be done.

3.3.2. Rancimat test with a procedure specially modified for thermal stability evaluation [20]

The Rancimat apparatus has also been adopted to measure thermal stability by not using an airflow and measurement of polymer content in an 8 g sample after 6 h at 200 °C [20,58]. A more traditional test for thermal stability, ASTM D6468, requires heating the sample at 150 °C for either 90 or 180 min. The sample is then cooled and either filtered to determine filterables via a total reflectance meter or gravimetrically in a manner similar to ASTM D227490. The modified Rancimat test is suitable for use in terms of repeatability and it is easy to handle [58].

3.3.3. TGA/DTA method

Thermal stability of oils depends on their chemical structures. Oils with a high proportion of unsaturated fatty acids are less stable than the saturated ones [66]. In the recent years, thermal analysis was successfully used to study the physical properties, chemical reaction and the thermal stability of oils. Thermo analytical methods, especially, thermogravimetry analysis (TGA) has the advantages of being precise, sensitive and fast needing small amount of sample [66].

Thermo analytical methods include a group of techniques in which the thermal behavior or thermal properties of a material are determined as a function of temperature. The thermal tests measure the change of weight and enthalpy as the sample is heated. TGA has been extensively used in polymer science for measurement of degradation of polymer [67–69]. The equipment continuously monitors the loss of sample weight while the sample is heated in isothermal or dynamic conditions. Thermal analysis techniques have been used for the characterization of edible oils and fats by studying several properties such as thermo-oxidative behavior and stability [70–72], specific heat [73], thermal decomposition activation energy [74], temperature and enthalpy of crystallization [75–78], effect of antioxidants on thermal stability of oils [74,79], degree of unsaturation from melting and crystallization oil profile curves [80] and high-pressure oxidation induction period measurements [81].

Thermogravimetric analysis is normally carried out either in the presence of air or in an inert atmosphere, e.g., N_2, He, Ar and the weight loss is recorded as a function of increasing temperature. The measurements are, sometimes, performed in O_2 atmosphere (1–5% O_2 in N_2 or He) and sometimes in a lean oxygen atmosphere (1–5% O_2 in N_2 or He) to slow down the oxidation process. Some instruments also record the temperature difference between the sample and one or more reference pans (differential thermal analysis or DTA) or the heat flow into the sample pan compared to that of the reference pan (differential scanning calorimetry, or DSC). The later can be used to monitor the energy released or absorbed via chemical reactions during the heating process.

In most cases, TGA analysis is performed in an oxidative atmosphere (air or oxygen and inert gas mixtures) with a linear temperature ramp. The maximum temperature is selected so that the sample weight is stable at the end of the experiment, implying that all chemical reactions have been completed.

The onset temperatures (T_{on}) as shown in Fig. 4 can be used to indicate the resistance of the oil to thermal degradation determined by extrapolating the horizontal baseline at 1% degradation. The intercept of this line with the tangent to the downward portion of the weight curve was defined as the onset temperature. As the oil is oxidized, its onset temperature decreases [66].

Table 1 is representing the comparison of different test methods available for different type of stabilities.

The above table summarizes the methods of various stabilities carried out by various researchers. The oxidation, thermal and storage stability of biodiesel has been determined by using various methods which includes Active oxygen method, ASTM D2274, ASTM D3241, EN 14112, ASTM D5483, ASTM D4625-04, ASTM D5304-06, ASTM D 6468-08, Modified Rancimat, TGA/DTA based on various stability parameters such as PV, AV, viscosity, tocopherols contents, OSI, total insolubles, filterable insolubles, adherent insolubles, linoleic acid contents, insolubles, onset temperature, enthalpy of crystallization, oxidation induction time, etc.

From the above table, it is concluded that the most useful and beneficial method for oxidation stability is EN 14112 method, which is not only less time consuming but also chances of error is very less with good repeatability. Also the method is compared with ASTM D2274 which is a standard test method to measure the oxidation stability. Modified Rancimat test for storage stability is found to be a useful method for storage stability with less time consuming, less error and good repeatability. Specifications are also available in international as well as national standards for Rancimat test. For thermal stability TGA/DTA and modified Rancimat test are found to be more appropriate. However, no specification is available in national and international standard for thermal stability.

The most effective test parameter is the induction period for oxidation stability, viscosity, linoleic acid contents, AV, onset temp and order of reaction for thermal stability and viscosity, induction period for storage stability. But no perfect correlation has been found between these stability parameters. Therefore, there is a need to develop co-relations between various stability parameters of vegetable oil and to study the effect of Rancimat induction period on various stability parameters e.g. insoluble formation, viscosity, linoleic acid contents, onset temperature, order of reaction, etc. The results of such studies would prove to be valuable to develop correlations between the various stabilities of oils and their biodiesels and effect of various parameters on the oxidation, thermal as well as storage behavior.

4. Conclusion

From the various experiments, it is concluded that two test methods emerges the most likely choice for the purpose of measurement of oxidation stability of biodiesel. These are ASTM 2274 and 743 Rancimat test. A comparison between these two shows that these may be used alternatively. The test methods were evaluated for their ease of use, applicability to the measurement of biodiesel, ability to discern additive effects and ability to discriminate between biodiesel samples of various levels of oxidation stability. Most commonly used methods to investigate the thermal stability are Rancimat test, ASTM D 6408-08, D 5304-06 and TGA/DTA. Rancimat test has been suggested as an important method to measure the thermal stability of oils, fats and biodiesel fuels. Further, the modified Karl Fischer (KF)

Coulometer has also been suggested as suitable method to measure the thermal as well as oxidation stability of vegetable oils. Large numbers of studies were devoted to the thermal stability of different oils using these methods. Further, TGA/DTA has been found as an effective method to check the deterioration of oil with respect to temperature using activation energy and order of reaction as the parameter to monitor the deterioration of oil. No co-relation have, however, been found in the literature between the results of various test methods. Much effort are required to be done in the field of biodiesel, especially to increase the thermal/oxidation stability of biodiesel produced from non-edible oils. Also the effect of blending of biodiesel with diesel on thermal stability needs to be investigated in details. The effect of thermal parameters on storage and oxidation stability is, therefore, an important R&D area to enhance and improve the biodiesel stability for use in existing engines as a substitute of petroleum diesel.

Acknowledgement

The authors greatly acknowledge the financial support from Ministry of New and Renewable Energy, Govt. of India in the form of research scholarship to carry out this work.

References

[1] Miyashita K, Takagi T. Study of the oxidative rate and prooxidant activity of free fatty acids. Journal of the American Oil Chemists' Society 1986;63(10): 1380–4.
[2] Pr EN 14103. Oil and fat derivatives. Fatty acid methyl esters (FAME). Determination of ester and linolenic acid contents; 2003.
[3] Bondioli P, Gasparoli A, Bella LD, Taghliabue S, Toso G. Biodiesel stability under commercial storage conditions over one year. European Journal of Lipid Science and Technology 2003;105:735–41.
[4] Isbell TA, Abbott TP, Carlson KD. Oxidative stability index of vegetable oils in binary mixtures with meadowfoam oil. Industrial Crops and Products 1999;9:115–23.
[5] Tian K, Dasgupta PK. Determination of oxidative stability of oils and fats. Analytical Chemistry 1999;71(9):1692–8.
[6] Knothe G, Dunn RO. Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals. Journal of the American Oil Chemists' Society 2003;80(10):1021–6.
[7] Knothe G. Structure indices in FA chemistry. How relevant is the iodine value? Journal of the American Oil Chemists' Society 2002;79(9):847–54.
[8] Page BD. High-performance liquid chromatographic determination of seven antioxidants in oil and lard: collaborative study. Journal – Association of Official Analytical Chemists 1983;66(3):727–45.
[9] Vuilleumier JP, Keller HE, Gysel D, Hunziker F. Clinical chemical methods for the routine assessment of the vitamin status in human populations. Part I: The fat-soluble vitamins A and E, and beta-carotene. International Journal for Vitamin and Nutrition Research 1983;53(3):265–72.
[10] Yao F, Dull G, Eitenmiller R. Tocopherol quantification by HPLC in pecans and relationship to kernel quality during storage. Journal of Food Science 1992;57:1194–7.
[11] Andersson K, Lingnert H. Influence of oxygen and copper concentration on lipid oxidation in rapeseed oil. Journal of the American Oil Chemists' Society 1998;75(8):1041–6.
[12] Mannino S, Buratti S, Cosio MS, Pellegrini N. Evaluation of the antioxidant power of olive oils based on a FIA system with amperiometric detection. Analyst 1999;124:1115–8.
[13] Brand-Williams W, Cuvelier ME, Berset C. Use of a free radical method to evaluate antioxidant activity. Lebensmittel-Wissenschaft und-Technologie 1995;28:25–30.
[14] Pellegrini N, Re R, Yang M, Rice-Evans CA. Screening of dietary carotenoids and carotenoid-rich fruit extracts for antioxidant activities applying the 2,2′-azonobis(3-ethylenebenzothiazoline-6-sulfonic) acid radical cation decolorization assay. Methods in Enzymology 1999;299:379–89.
[15] Khatoon S, Krishna AGG. Assessment of oxidation in heated safflower oil by physical, chemical and spectroscopic methods. Journal of Food Lipids 1998;5:247–67.
[16] DuPlessis LM, DeVilliers JBM, Van der Walt WH. Journal of the American Oil Chemists' Society 1985;62(4):748–52.
[17] Miyashita K, Takagi T. Study of the oxidative rate and prooxidant activity of free fatty acids. Journal of the American Oil Chemists' Society 1986;63(10): 1380–4.
[18] Monyem A, Canakci M, Van Gerpen J. Investigation of biodiesel thermal stability under simulated in-use conditions. Applied Engineering in Agriculture 2000;16(4):373–8.
[19] Mittelbach M, Gangl S. Long storage stability of biodiesel made from rapeseed and used frying oil. Journal of the American Oil Chemists' Society 2001;78(6):573–7.
[20] Stability of biodiesel used as a fuel for diesel engines and heating systems, Presentation of BIOSTAB project results, Graz, Austria; July 3, 2003.
[21] Blekas G, Tsimidou M, Boskou D. Contribution of alpha-tocopherol to olive oil stability. Food Chemistry 1995;52(3):289–94.
[22] Johnson OC, Kummerow FA. Chemical changes which take place in an edible oil during thermal oxidation. Journal of the American Oil Chemists' Society 1957;34:407–9.
[23] Raghuveer KG, Hammond EG. The influence of glyceride structure on the rate of autooxidation. Journal of the American Oil Chemists' Society 1967;44:239–43.
[24] Halliwell B. Oxygen radicals: a commonsense look at their nature and medical importance. Medical Biology 1984;62:71–7.
[25] EN ISO 6885: 2000. Animal and vegetable fats and oils. Determination of anisidine value.
[26] Holm U, Ekbom K, Wode G. Determination of the extent of oxidation of fats. Journal of the American Oil Chemists' Society 1957;34:606–9.
[27] Neff WE, Selke E, Mounts TL, Rinsch EN, Zeitoun MAM. Effect of triacylglycerol composition and structures on oxidative stability of oils from selected soybean germplasm. Journal of the American Oil Chemists' Society 1992;69(2): 111–8.
[28] Neff WE, El-Agaimy MA, Mounts TL. Oxidative stability of blends and interesterified blends of soybean oil and palm olein. Journal of the American Oil Chemists' Society 1994;71(10):1111–6.
[29] Konishi H, Neff WE, Mounts TL. Oxidative stability of soybean oil products obtained by regioselective chemical interesterification. Journal of the American Oil Chemists' Society 1995;72(11):1393–8.
[30] Hari Krishna S, Manohar B, Divakar S, Karanth NG. Lipase-catalyzed synthesis of isoamyl butyrate: optimization by response surface methodology. Journal of the American Oil Chemists' Society 1999;76(12):1483–8.
[31] Sherwin ER. Oxidation and antioxidants in fat and oil processing. Journal of the American Oil Chemists' Society 1978;55:809–14.
[32] Bondioli P, Gasparoli A, Lanzani A, Fedeli E, Veronese S, Sala M. Storage stability of biodiesel. Journal of the American Oil Chemists' Society 1995;72(6):699–702.
[33] Peled M, Gutfinger T, Letan A. Effect of water and BHT on stability of cottonseed oil during frying. Journal of the Science of Food and Agriculture 1975;26:1655–66.
[34] Asap T, Augustin MA. Effect of TBHQ on quality characteristics of RBD olein during frying. Journal of the American Oil Chemists' Society 1986;63(9):1169–72.
[35] Chang SS, Kummerow FA. The isolation and characterization of the polymers formed during the autoxidation of ethyl linoleate. Journal of the American Oil Chemists' Society 1953;30:403–7.
[36] Chang SS, Kummerow FA. The relationship between the oxidative polymers of soybean oil and flavor reversion. Journal of the American Oil Chemists' Society 1954;30:324–7.
[37] Kalbag SS, Narayan KA, Chang SS, Kummerow FA. Polarographic studies of fat oxidation. Journal of the American Oil Chemists' Society 1955;32:271–4.
[38] Bondioli P, Gasparoli A, Bella LD, Tagliabue S. Evaluation of biodiesel storage stability using reference methods. European Journal of Lipid Science and Technology 2002;104:777–84.
[39] Canakci M, Monyem A, Van Gerpen J. Accelerated oxidation processes in biodiesel. Transactions on ASAE 1999;42:1565–72.
[40] Dunn RO. Effect of oxidation under accelerated conditions on fuel properties of methyl soyate (biodiesel). Journal of American Oil Chemists' Society 2009;79:915–20.
[41] Knothe G, Steidley KR. Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. Fuel 2005;84:1059–65.
[42] Yuan W, Hansen AC, Zhang Q, Tan Z. Temperature-dependent kinematic viscosity of selected biodiesel fuels and blends with diesel fuel. Journal of the American Oil Chemists' Society 2005;82(3):195–9.
[43] Jain S, Sharma MP. Stability of biodiesel and its blends: a review. Renewable and Sustainable Energy Review 2010;14(2):667–78.
[44] AOCS Official and Tentative Methods: Cd 12-57, Fat stability-active oxygen method (AOM) reapproved; 1997.
[45] Morris SG, Magidman P, Luddy FE, Riemenschneider RW. Beef tallow in shortening preparations. Journal of the American Oil Chemists' Society 1956;33:353–5.
[46] Sherwin ER. Antioxidants for food fats and oils. Journal of the American Oil Chemists' Society 1971;49(8):468–72.
[47] Sherwin ER, Luckadoo BM. Studies on antioxidants treatment of crude vegetable oils. Journal of the American Oil Chemists' Society 1970;47:19–23.
[48] Laubli MW, Bruttel PA. Determination of the oxidative stability of fats and oils: comparison between the active oxygen method (AOCS Cd 12-57) and the Rancimat method. Journal of the American Oil Chemists' Society 1986; 63(6):792–5.
[49] Hill SE, Perkins EG. Determination of oxidation stability of soybean oil with the oxidative stability instrument: operation parameter effects. Journal of the American Oil Chemists' Society 1995;72(6):741–3.
[50] Standard test method for oxidation stability of distillate fuel oil (accelerated method). Modified, specifically for use with biodiesel by NREL, USA, ASTM standard.

[51] Stavinoha LL, Howell S. Potential analytical methods for stability testing of biodiesel and biodiesel blends. SAE Paper 1999-01-3520; 1999.
[52] Standard test method for thermal oxidation stability of aviation turbine fuels (JFTOT procedure), ASTM standard D 3241.
[53] Determining the oxidation stability of biodiesel, European standard EN 14112.
[54] Sareen R, Sharma M, Sinharay S, Malhotra RK. Jatropha-Palm biodiesel blends: an optimum mix for Asia. Fuel 2007;86(10–11):1365–71.
[55] Das LM, Bora DK, Pradhan S, Naik MK, Naik SN. Long-term storage stability of biodiesel produced from Karanja oil. Fuel 2009. doi: 10.1016/j.fuel.2009.05.005.
[56] Hasenhuettle GL, Hartel RW. Food emulsifiers and their applications. New York: Chapman and Hall; 1997.
[57] Westbrook SR. An evaluation and comparison of test methods to measure the oxidation stability of neat biodiesel. San Antonio, Texas: Southwest Research Institute; September 2003–May 2005.
[58] Berthiaume D, Tremblay A. Study of Rancimat test method in measuring the oxidation stability of biodiesel ester and blends. Oleotek Inc.; November 2006.
[59] Standard test method for oxidation induction time of lubricating greases by pressure differential scanning calorimetry, ASTM Standard D5483-05.
[60] Dunn RO. Analysis of oxidative stability of methyl soyate by pressurized-differential scanning calorimetry (P-DSC). ASAE Transaction 2000;43(5):1203–8.
[61] Tan CP, Che Man YB. Recent developments in differential scanning calorimetry for assessing oxidative deterioration of vegetable oils. Trends IN Food Science and Technology 2002;13:312–8.
[62] Cheenkachorn K, Perez JM, Lloyd WA. Use of pressurized differential scanning calorimetry (PDSC) to evaluate effectiveness of additives in vegetable oil lubricants. In: Spring technical conference. Saltzburg, Austria: Internal Combustion Engine Division; May 11–15, 2003.
[63] Standard test method for middle distillate fuel storage stability at 43 °C (110 °F), ASTM standard D4625-04.
[64] Standard test method for assessing middle distillate fuel storage stability by oxygen overpressure, ASTM standard D 5304-06.
[65] Standard test method for high temperature stability of middle distillate fuels, ASTM standard D 6468-08.
[66] Wan Nik WB, Ani FN, Masjuki HH. Thermal stability evaluation of palm oil as energy transport media. Energy Conversion and Management 2005;46:2198–215.
[67] Wilkie CA. TGA/FTIR: an extremely useful technique for studying polymer degradation. Polymer Degradation and Stability 1999;66(3):301–6.
[68] Fornes TD, Yoon PJ, Paul DR. Polymer matrix degradation and color formation in melt processed nylon 6/clay nanocomposites. Polymer 2003;44(24):7545–56.
[69] Li XH, Meng YZ, Zhu Q, Tjong SC. Thermal decomposition characteristics of poly(propylene carbonate) using TG/IR and Py-GC/MS techniques. Polymer Degradation and Stability 2003;81(1):157–65.
[70] Buzás I, Simon J, Holló J. Study of the thermooxidative behavior of edible oils by thermal analysis. Journal of the American Oil Chemists' Society 1979;56:685–8.
[71] Roos YH. Thermal analysis, state transitions and food quality. Journal of Thermal Analysis and Calorimetry 2003;71(1):197–203.
[72] Magoshi J, Becker MA, Han Z, Nakamura S. Thermal properties of seed proteins. Journal of Thermal Analysis and Calorimetry 2003;70(3):833–9.
[73] Kowalski B. Determination of specific heats of some edible oils and fats by differential scanning calorimetry. Journal of Thermal Analysis 1988;34(5–6):1321–6.
[74] Kowalski B. Thermal-oxidative decomposition of edible oils and fats DSC studies. Thermochimica Acta 1991;184(1):49–57.
[75] Gloria H, Aguilera JM. Assessment of the quality of heated oils by differential scanning calorimetry. Journal of Agricultural and Food Chemistry 1998;46(4):1363–8.
[76] Tan CP, Man YB. Differential scanning calorimetric analysis for monitoring the oxidation of heated oils. Food Chemistry 1999;67(2):177–84.
[77] Relkin P, Sourdet S, Fosseux PY. Fat crystallization in complex food emulsions. Journal of Thermal Analysis and Calorimetry 2003;71(1):187–95.
[78] Aktaş N, Kaya M. Detection of beef body fat and margarine in butterfat by differential scanning calorimetry. Journal of Thermal Analysis and Calorimetry 2001;66(3):795–801.
[79] Felsner ML, Matos JR. Analysis of the thermal stability and oxidation temperature of commercial edible oils by thermogravimetry. Anais da Associacao Brasileira de Quimica 1998;47(4):308–12.
[80] Tan CP, Man YB. Differential scanning calorimetric analysis of edible oils: comparison of thermal properties and chemical composition. Journal of the American Oil Chemists' Society 2000;77(2):143–55.
[81] Gimzewski E. A multi-sample high-pressure DTA for measuring oxidation induction times. Thermochimica Acta 1990;170:97–105.